Title: Pillared Clays as Superior Catalysts for Selective Catalytic Reduction of NO
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Selective catalytic reduction (SCR) of NO by NH_3 is presently performed with vanadia-based catalysts for flue gas applications. Hydrocarbons would be the preferred reducing agents over NH_3 because of the practical problems associated with the use of NH_3 (i.e., handling and slippage through the reactor). SCR of NO by hydrocarbon can also find important applications for lean-burn (i.e., O_2-rich) gasoline and diesel engines where the noble-metal three-way catalysts are not effective in the presence of excess oxygen.

The first catalysts found to be active for SCR of NO by hydrocarbons in the presence of oxygen were Cu^{2+} ion-exchanged ZSM-5 and other zeolites, reported in 1990 by Iwamoto in Japan and Held et al. in Germany. These reamin to be the most active and also most intensively studied catalysts.

Pillared interlayered clays (PILCs), or pillared clays, are two-dimensional zeolite- like materials prepared by exchanging the charge-compensating cations between the clay layers with inorganic hydroxycations followed by decomposition into metal oxide pillars of molecualr dimensions. The inter-layer and inter-pillar gallery spacings provide high surface areas and pore voids. In addition, they have high cation exchange capacities.

In this program, ion-exchanged pillared clays were studied as new catalysts for selective catalytic reduction (SCR) of NO by ethylene. Three most important pillared clays, Al_2O_3-PILC, ZrO_2-PILC and TiO_2-PILC, were synthesized. A commercially available pillared clay, Al_2O_3-Laponite, was also included in this study. Laponite is a synthetic hectorite. Cation exchanges were performed to prepare the following catalysts: Cu-Ti-PILC, Cu-Al-PILC , Cu-Zr-PILC, Cu-Al-Laponite, Fe-Ti-PILC, Ce-Ti-PILC, Ce-Ti-PILC, Co-Ti-PILC, Ag-Ti-PILC and Ga-Ti-PILC. All Cu^{2+} exchanged pillared clays showed higher SCR activities than Cu-ZSM-5. In particular, Cu-Ti-PILC showed the highest activities for SCR of NO than the other cation-exchanged pillared clay catalysts.

The SCR activities, in terms of NO conversion, for Cu^{2+} exchanged on pillared clays that were pillared by different metal oxide pillars are compared directly in Fig.1. Cu-Al-Laponite showed higher actvities at higher temperatures. For all pillared clay catalysts, the product selectivites were 100% for N_2, with no N_2O formation.

H_2O and SO_2 only slightly deactivated the SCR activity of Cu-Ti-PILC, whereas severe deactivation was observed for Cu-ZSM-5. Deactivation by SO_2 are shown in Fig. 2 for various catalysts. The deactivation by H_2O was very similar to that by SO_2.

The catalytic activity of Cu-Ti-PILC was found to depend on the method and amount of copper loading. The catalytic activity increased with copper content until it reached 245% ion exchange. The addition of 0.5 wt.% Ce_2O_3 into Cu-Ti-PILC increased the activities by about 10-30% while 1.0 wt.% of Ce_2O_3

decreased the activity of Cu-Ti-PILC due to pore plugging. Cu-Ti-PILC was found to be an excellent catalyst for NO SCR by NH_3, but inactive when CH_4 was used as the reducing agent.

One of the reasons for the high activities for the PILC catalysts was their large pores (or mesopores) as comapred with ZSM-5. Diffusion resistance was minimized in the mesopores. The new class of mesoporous molecular sieves, MCM-41, was also included in this study. Ion exchanged MCM-41 and Pt/MCM-41 showed promising activities. In particular, Cu-Al-MCM-41 and Pt/MCM-41 exhibited high hydrocarbon SCR activities and Fe^{3+} exchanged Al-MCM-41 was found to be an excellent ammonia SCR catalyst.

Active hydrocarbon SCR catalysts are also good reversible sorbents for NO_x. An alternative approach for SCR is to use an NO_x trap. This trap must selectively adsorb NO (in O_2) in combustion gases and the adsorption must be reversible. We have developed an effective sorbent, i.e., sulfated TiO_2, for reversible chemisorption of NO_x.
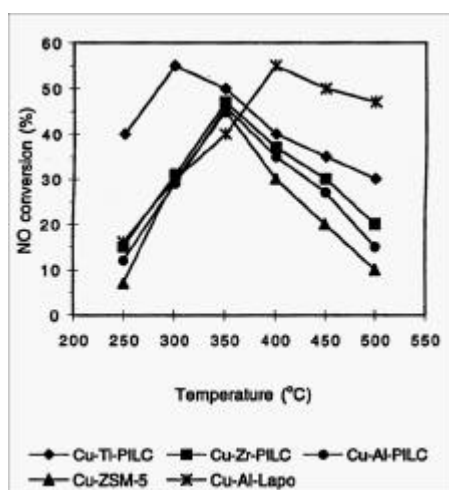

Fig. 1. SCR activities of Cu-Ti-PILC, Cu-Zr-PILC, Cu-Al-PILC, Cu-Al-Laponite and Cu-ZSM-5 for NO reduction by ethylene. Reaction conditions: NO = C_2H_4 = 1000 ppm, O_2=2%, catalyst = 0.5 g, He = balance and total flow rate =250 cc/min.   Note that Cu-ZSM-5 was the most active and has been the most extensively studied catalyst.
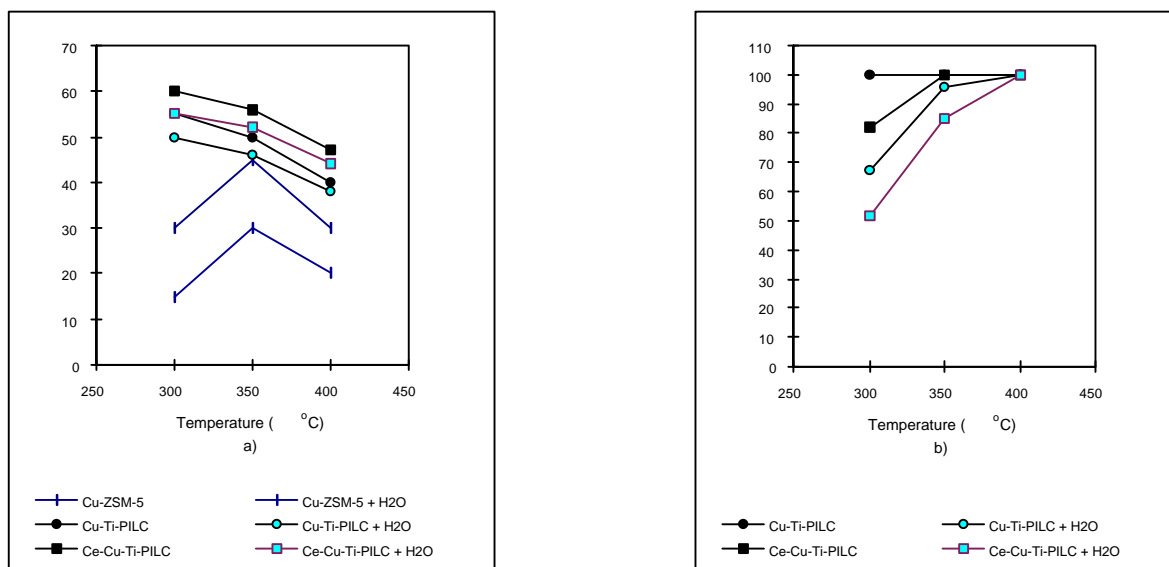
Fig. 2. SO$_2$ effect on SCR of NO by ethylene with Cu-Ti-PILC: a) % NO conversion and b) % C$_2$H$_4$ conversion. Reaction conditions: NO = C$_2$H$_4$ = 1000 ppm, O$_2$ = 2%, SO$_2$ = 500 ppm, catalyst = 0.5 g, He = balance and total flow rate = 250 cc/min.

<u>Publications</u>

R.T. Yang, T.J. Pinnavaia, W. Li and W. Zhang, "Fe^{3+} Exchanged Mesoporous Al-HMS and Al-MCM-41 Molecualr Sieves for Selective Catalytic Reduction of NO with NH_3 , " Journal of Catalysis, 172, 488 (1997).

M. Sirilumpen, R.T. Yang and N. Tharapiwattananon, "Selective Catalytic Reduction of NO with Hydrocarbon on Cu2+-Exchanged Pillared Clays: An IR Study of the NO Decomposition Mechanism," Journal of Molecular Catalysis, in press.

R. Long and R.T. Yang, "Pt/MCM-41 Catalyst for Selective Catalytic Reduction of NO with Hydrocarbons in the Presence of Excess Oxygen," Catalysis Letters, in press.

R.T. Yang, W. Li and N. Chen, "Reversible Chemisorption of NO in the Presence of O2 on Titania and Titania Modified with Surface Sulfate," Applied Catalysis, in press.

R. Long and R.T. Yang, "Selective and Reversible Adsorbents for Nitic Oxide from Hot Combustion Gases," in Adsorption and Its Application in Industry and Environmental Protection (Ed. A. Dabrowski), Elsevier, Amsterdam (1998).